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Synthesis of MCM-41 with Different Pore Diameters without Addition of Auxiliary Organics

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Swollen and highly ordered MCM-41 type materials with varied pores sizes, but with similar wall thicknesses, have been directly synthesized in the absence of auxilliary organics by controlling the preparation conditions. The most important parameter in the synthesis in order to control the pore opening is the cetyltrimethylammonium ($CTMA^+$) concentration in the synthesis gel. Our results suggest that the mechanism of swelling is related with the replacement of some $CTMA^+$ species by others cations in the interface formed between the liquid crystal and the silica surfaces. This approach could open new insights into the mechanism of formation of MCM-41 type materials as well as having in addition an important impact on the preparation of large mesoporous materials.

The recent synthesis and investigation of a new family of silica-based mesoporous materials designated as M41S have attracted great interest because they expand typical molecular sieves into the extra-large-pore range which generates the potential for the applications of these materials in catalysis, separation, and sorption for very bulky molecules.[1−5] The use of surfactants plays an extremely important role in the synthesis of these solids due to a self-assembly process to form the mesoporous materials.[2,6,7] Mobil researchers have announced in their earlier work that the pore size of the M41S can be tailored between 15 and 100 Å by using surfactants with variable chain length and by addition of swelling organic compounds such as trimethylbenzene or others to the synthesis mixture.[2,8] Typically, the mesoporous materials synthesized in the presence of swelling organic compounds exhibited a proportional increase in *d* spacing of the X-ray (100) reflection with incremental addition of the organic swelling agent and so a larger quantity of auxilliary organics was required to form the mesoporous materials with the enlarged pores (greater than 45 Å). For instance, to obtain a MCM-41 type material with an unit cell of 75 Å using trimethylbenzene as swelling compound, ~20 wt % of aromatic has to be introduce into the gel composition.[8] It is obvious that the introduction of large amounts of organics in order to swell the original liquid crystals is not an optimum procedure, since their use involves not only a larger reaction volume, but also additional processes for separation and recycling of the organic swelling compounds. It is evident that it would be highly desirable to be able to increase and to control the pore size of the mesoporous materials without introducing organic swelling agents. If this was achieved it would have an important impact on the preparation of the MCM-41 type materials. Recently, Ozin et al.[9] have found that the swollen processes including the lattice parameters and the pore size could be achieved by using postsynthesis approach. However, from the results showed in this article it is evident that the wall thickness increases during the postsynthetic treatment, while only a minor increment in the pore size (~7 Å) is observed. Similar results have been reported by Klinowski et al.[10] by using a direct synthesis method. Effectively, the maximum increment in the pore size observed by Klinowski was only around 10 Å that is a rather modest value when compared to those obtained by using organic swelling agents. Here we report a new route to directly swell the pore of MCM-41 during the synthesis by adjusting the composition of reaction mixtures and controlling the crystallization variables without addition of auxilliary organics. The resultant mesoporous materials have constant wall thickness and pore sizes comparable to those generated by use of organic swelling agents. On the basis of the results obtained a new cation-inclusive swelling mechanism is proposed.

Pure siliceous MCM-41 with different pore diameters were hydrothermally synthesized with the following

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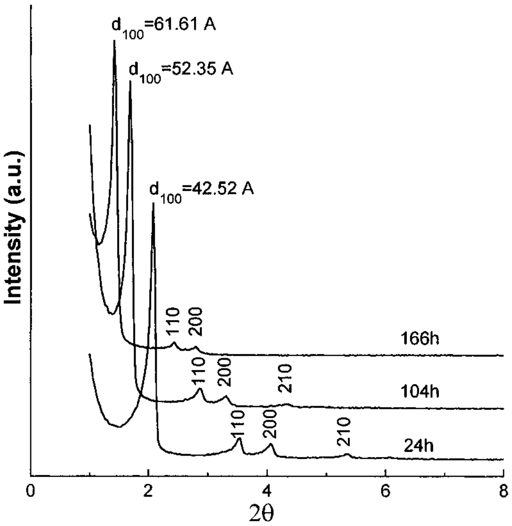

Figure 1. X-ray diffraction patterns of MCM-41 and swollen derivatives synthesized with CTMABr/SiO$_2$ = 0.12 in the presence of TMA$^+$ at 150 °C for different crystallization times.

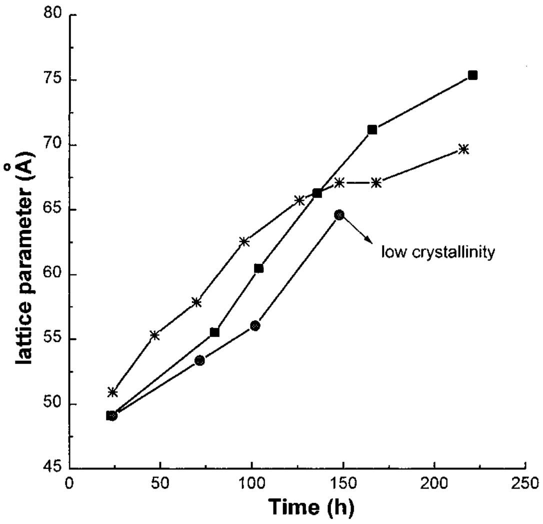

Figure 2. Relationship of a_0 parameter of mesoporous materials with crystallization times. (synthesized with CTMA/SiO$_2$ = 0.12 at 150 °C in the presence of (■) TMA$^+$, (*) TEA$^+$ and (●) Na$^+$, respectively).

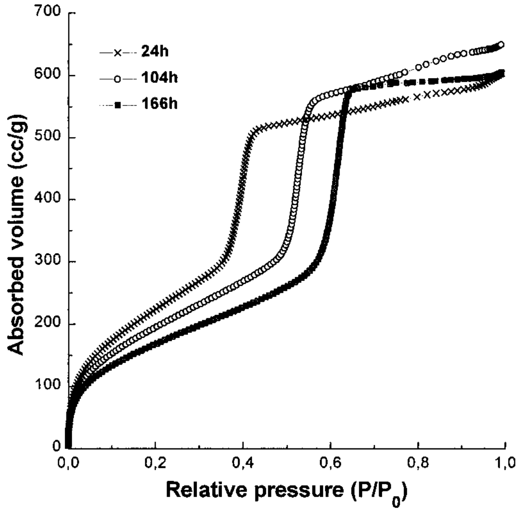

Figure 3. Ar adsorption isotherms of MCM-41 and swollen derivatives synthesized with CTMABr/SiO$_2$ = 0.12 at 150 °C for different crystallization times.

molar composition: SiO$_2$·xCTMABr·0.14M$_2$O·26.2H$_2$O, where x was varied between 0.06 and 0.15; M represents cations, such as tetramethylammonium (TMA$^+$), tetraethylammonium (TEA$^+$), or Na$^+$ that were added as hydroxides. In a typical synthesis, an aqueous solution of tetramethylammonium silicate obtained from the reaction between silica (Aerosil 200, Degussa) and tetramethylammonium hydroxide solution (25% TMAOH, 10% SiO$_2$), was added to an aqueous solution containing 9.86 wt % cetyltrimethylammonium bromide (CTMABr). Then, amorphous silica was added under continuous stirring. The homogeneous gel (pH ≈ 13.8) was sealed in Teflon-lined stainless steel autoclaves and heated at 150 °C under static conditions. The time of crystallization was varied from 1 to 10 days. The resulting solid products were recovered by filtration and then washed and dried at 60 °C for 24 h. The occluded organic was removed by heating the samples at 540 °C under a continuous flow of N$_2$ for 2 h, before a flow of air was passed at 540 °C for 6 h.

The X-ray diffraction patterns (obtained using a Phillips X'Pert diffractometer with Cu Kα radiation) of the as-synthesized samples (Figure 1) clearly show that a typical MCM-41 material with d_{100} = 42.5 Å is formed in the presence of TMA$^+$ cations when the crystallization time was 24 h. Longer crystallization time at 150 °C gradually shifts the X-ray d_{100} position to higher values. After 7–10 days of reaction a highly crystalline material exhibiting MCM-41 structure with an a_0 unit-cell parameter of 71.1–73.3 Å ($a_0 = 2d_{100}/\sqrt{3}$) was recovered (see Figure 1). When the crystallization time is prolonged beyond 10 days, a loss of crystallinity accompanied by a decrease in the pore volume of the mesoporous materials is observed. The relationship between the a_0 parameter of the as-synthesized samples and the crystallization time is shown in Figure 2. The sample with the largest swelling reaches a value for the a_0 parameter of 73.3 Å under the synthetic conditions described above. Upon calcination the intensity of the X-ray reflections increases and an unit-cell contraction of ~2.5 Å was observed for all the samples studied, in agreement with previously reported work on nonswollen MCM-41.[3,11]

Adsorption isotherms of argon and nitrogen were carried on a ASAP 2000 Micromeritics apparatus. As shown in Figure 3, the argon isotherms exhibit a gradual shift in the capillary condensation to higher relative pressure with increasing a_0 parameters (or crystallization times). This clearly indicates that the pore size of the mesoporous materials increases with the a_0 value since larger pores are filled at higher P/P_0.[12] The sharp step in the adsorption isotherms for the samples studied implies the uniformity in the pore-size distribution.[13] The N$_2$ adsorption isotherms have been used here to estimate the cylindrical pore size and surface area for the calcined samples with different lattice parameters, and the results are summarized in

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Table 1. Unit-Cell Parameter, Surface Area, Pore Size, and Wall Thickness of Calcined Samples[a]

sample	a_0 (Å)	surface area (m^2/g)	pore size (Å)[b]	wall thickness (Å)
1	47	937	39	8
2	54	809	46	8
3	57	801	50	7
5	68	753	59	9
6	75	731	66	9

[a] Samples were obtained from the following gel composition: SiO_2:0.12CTMABr 0.14TMA$_2$O: 26.2H_2O. [b] Pore size calculated assuming a multilayer thickness correction.[14]

Table 2. Effect of the Temperature of Crystallization and the Stirring Rate during Synthesis in the Lattice Parameter[a]

sample	temp of crystallization (°C)	crystallization time (h)	stirring rate (rpm)	lattice parameter (Å)
13	135	1200	static	64.4
4	150	136	static	66.3
14	175	14	static	70.4
15	135	720	static	59.0
16	135	168	60	59.2

[a] Samples were obtained from the following gel composition: SiO_2:0.12CTMABr: 0.14TMA$_2$O: 26.2H_2O.

Table 1. It is observed that the pore sizes of the studied samples proportionally increase as the a_0 parameters enlarge, while the surface area of the samples gradually decreases. The pore sizes of the samples swelled under the conditions described here may be over 66 Å. Moreover, the wall thickness calculated by subtracting the pore diameter from the a_0 parameter value is basically constant.

Among the parameters of synthesis studied in this work, the most important has been found to be the CTA^+ concentration in the synthesis mixture. Indeed, by working at a CTA^+/SiO_2 ratio between 0.09 and 0.15, we were able to produce highly crystalline MCM-41 type materials with a pore size in the highest range of those stated in the original Mobil patent,[8] but avoiding the use of any swelling organic compound into the synthesis gel. On the other hand, the values of pore diameter reported here are 20−30 Å larger than those published previously by Klinowski[10] or Ozin.[9] CTA^+/SiO_2 ratios below 0.09 speed the swelling rate, but poorly crystalline MCM-41 materials are produced. Finally, by increasing CTMA/SiO_2 ratio to 0.20 results in the formation of mesoporous material with distribution a bimodal pore distributions with two major channel opening centered at 44 and 48 Å. To obtain a swollen, uniformed, and well-crystallized mesoporous material, the optimum range of CTMA/SiO_2 ratios is found to be between 0.09 and 0.15.

Another important factor that influences the swelling process is crystallization temperature. Effectively, as shown in Table 2 a strong increase in the swelling rate is observed by increasing the temperature of crystallization to 175 °C. At this temperature, a crystallization time as short as 14 h produces a MCM-41 type solid with an unit cell of 70 Å which is larger than that obtained at 135 °C after 50 days of heating ($a_0 = 64.4$ Å for sample 13 in Table 2). Moreover, when the synthesis is carried out under dynamic conditions (sample 16 in Table 2), that is, when the autoclaves were rotated at 60 rpm, a benefit in the swelling process is observed being the swelling completed after 1 week at 135 °C instead of the 1 month necessary under static conditions.

The nature of the silica layer in the swollen materials has been studied by means of ^{29}Si MAS NMR. Only slight differences have been observed between the swollen samples compared to the nonswollen materials being the $Q_3/(Q_4 + Q_3)$ ratio close to 0.5 for all the as-prepared samples. This ratio decreases to 0.25 during the calcination process similarly to that observed in the nonswollen materials. Then, we can conclude that the degree of polymerization of the oligomers of silica practically does not change during the swelling process.

The swelling process is also observed by replacing TMA^+ in the gel by TEA^+ or even by inorganic cations such as Na^+ (Figure 2). Nevertheless, the swelling rate and the final a_0 value strongly depends on the nature of the cations apart from $CTMA^+$ present in the gel. In fact, Na^+ seems to give less stable mesoporous materials and with a lower swelling rate than those obtained in the presence of tetraalkylammonium cations (TAA^+).

Elemental and chemical analyses confirm that the TMA^+, TEA^+, or Na^+ cations are incorporated in the mesoporous products during the synthesis, although Na^+ is included into the final solid in a lower molar fraction than the others. The obtained results are listed in Table 3. It is notable that the swelling of mesoporous materials is always accompanied by a gradual increase in the content of TAA^+ cations but a with slight decrease of the $CTMA^+$ content. Thus, the larger the pore, the higher the content of cations in the products is. This result may indicate that the swelling mechanism, although not well understood at the moment, seems to be related to the replacement of some $CTMA^+$ cations

Table 3. Lattice Parameter and Content of Surfactant and Cations of the As-Synthesized MCM-41 and Swollen Derivates Samples[a]

			content of surfactant and cations (mmol/g)					cation-to-surfactant ratio	
sample	crystallization time (h)	a_0(Å)	CTMA	TMA	TEA	CTMA+TMA	CTMA+TEA	TMA/CTMA	TEA/CTMA
1	24	49.1	1.313	0.092		1.405		0.070	
2	80	55.5	1.301	0.149		1.450		0.115	
3	104	60.4	1.280	0.214		1.494		0.167	
4	136	66.3	1.266	0.230		1.496		0.182	
5	166	71.1	1.234	0.281		1.515		0.228	
6	221	75.3	1.246	0.281		1.527		0.226	
7	24	50.9	1.341		0.054		1.395		0.040
8	47	55.3	1.298		0.076		1.374		0.059
9	70	57.9	1.295		0.071		1.366		0.055
10	96	62.5	1.292		0.085		1.377		0.066
11	168	67.1	1.244		0.112		1.356		0.090
12	216	69.7	1.149		0.180		1.329		0.157

[a] Samples were obtained from the following gel composition: SiO_2:0.12 CTMABr:0.14 TAA$_2$O:26.2 H_2O.

by TAA^+ in the interface formed between the liquid crystal and the silica surfaces. Indeed, it is noticeable that the decrease of $CTMA^+$ content observed during the swelling process is larger in the case where TEA^+ is used instead of TMA^+ in the gel composition, although the molar fraction of the former cation is lower in the solid. It appears that the bulkier TEA^+ cation expels out more effectively the $CTMA^+$ from the interface than the smaller TMA^+ cations.

The above analysis of swelling mechanism is different from that proposed by Ozin et al.[9] in their observed swelling during a postsynthesis treatment. They claimed that the additional space due to the pore-size enlargement was filled by extra water which sheaths the liquid-crystal template since an important increment of water amount was found after the enlargement of pore size by postsynthesis. However, in our case only little amount of water is detected by TG-MS and no significant variation is observed during the swelling process, indicating that in our conditions the swelling is mainly due to the incorporation of TAA^+ in the micelle as we discussed above.

In addition, the same approach has been successfully extended to Al- and Ti-substituted MCM-41, and further investigations on these materials and the mechanism of swelling are in progress.

In conclusion, we would like to emphasize that swollen, uniform and well-crystallized mesoporous MCM-41 type materials have been directly obtained without addition of auxilliary organics by adjusting surfactant CTMABr concentration in the presence of small cations such as TMA^+, TEA^+, or Na^+ and controlling the crystallization variables. These results not only have an important impact on the preparation of larger pore mesoporous materials, but also open new insights into the mechanism of formation of these materials.

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